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SOVIET STUDIES ON POWDER METALLURGY

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## SOVIET STUDIES ON POWDER METALLURGY

Following is the translation of four articles in the Russian-language book Issledovaniya po zharoprochnym splavam, (Research on Heat-Resistant Alloys), Vol IV, Publishing House of the Academy of Sciences USSR, Moscow, 1959. Complete bibliography information accompanies each article.

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## INVESTIGATION OF DIFFUSION CREEP IN POWDER METAL BODIES

Following is a translation of an article by B. Ya. Pines and A. F. Sirenko in the Russian-language book Issledovaniya po zharoprochnym splavam, (Research on Heat-Resistant Alloys), Vol 4, Publishing House of the USSR Academy of Sciences, Moscow, 1959, pages 301-310.

We know that in powder metal bodies (prepared by compression of metallic powders) at high temperatures processes of sintering occur at a marked rate, which can be viewed as a phenomenon of "diffusion creep" under the influence of surface tension [1]. Because of this powder metal bodies are an interesting subject for the study of creep phenomena, for here it is possible to compare creep phenomena which are conditioned by: a) external forces, and b) surface tension operation on surfaces of internal pores. In addition it is essential to elucidate the laws governing creep for nonequilibrium conditions, in many cases characteristic for powder metal bodies, as well as to investigate creep in heterogeneous bodies having a distinct previously imposed heterogeneity.

At the present time there is no complete clarity as to the mechanism of creep in metals and alloys. It is possible that at various regions of temperature and at various stresses a different mechanism of creep formation is operating; apparently there is a "dislocation" and a "diffusion" creep [2, 3]. [See Note]

[Note]: Here it is not taken into consideration that diffusion creep may be achieved by volumetric autodiffusion (viscous flow) and by diffusion along grain boundaries (as in the famous experiments of Ke Tin-<sup>4</sup> on internal friction). The activation energies differ in the two cases [9].)

In order to approximate conditions of "diffusion creep" (in which deformation is conditioned by the flow of the set autodiffusion of atoms) in this investigation tests were conducted at relatively high temperatures and small applied loads. Test materials were samples from copper powder produced electrolytically, nickel carbonyl and "vertex" iron as well as from mixtures of these powders. The grain size of Cu and Ni powder was 10-15

microns, of Fe powder --- 30-40 microns. The samples were executed in the shape of rods of square cross-section  $3 \times 3 \text{ mm}^2$  and working length of 90 mm, having a special butt of larger cross-section. The rods were prepared by pressing the respective powders (or their mixtures) in a dismountable press mold. Initial porosity of the samples in all non-specified cases was 30-32%. Tests were done at temperatures up to  $1250^\circ$  in a vacuum apparatus which was evacuated with the M-M-40 oil diffusion pump. The samples were subjected to strain in which the load was brought about with an electromagnet. The clamps in which the butt ends of a sample were braced were made of stainless steel and had a cross-section one and a half orders greater than the cross-section of the samples and therefore were not deformed. Sample elongation was recorded by the angle of rotation of a speculum through whose bracing axis a filament was placed connected to the lower movable clamp of the butt end of the sample and stretched by a small weight. The light from the speculum, focused with a lens, was read on a scale standing 1.5 meters away. The total magnification in the measurement of displacement caused by deformation was  $\sim 800$ . Two specula were used simultaneously for the fixation of deformation creep as well as contraction of the sample due to sintering. A change in the beginning reading for the lights from the specula could be produced during the test and was achieved by turning them (to the angle desired) by means of "screw drivers" introduced through rubber packing into the space of the vacuum device, which moved in when necessary for engagement with the axes of the specula and which were withdrawn after a turn.

Figure 1 shows curves of creep elongation with time for various samples at temperatures of  $1000^\circ$  and  $1100^\circ$ . The curves of figure 1a refer to samples of pure copper at  $1000^\circ$  under a load of  $10 \text{ gm/mm}^2$ . The various curves correspond to samples which have undergone preliminary annealing of different duration  $\tau$  at the same temperature. Curves of samples subjected to short-term preliminary annealing ( $\tau \leq 15 \text{ min.}$ ) (fig. 1b, c, d), have the shape of typical "creep" curves. At first there occurs a stage of relatively rapid, unsteady creep whose rate decreases with time. Then follows a stage of "steady" creep occurring at a practically constant rate. As we know, yet a third stage of creep precedes the disruption of the samples, during which phase deformation is accelerated. This stage is absent in figure 2, apparently due to the inadequate duration of the test at small loads.

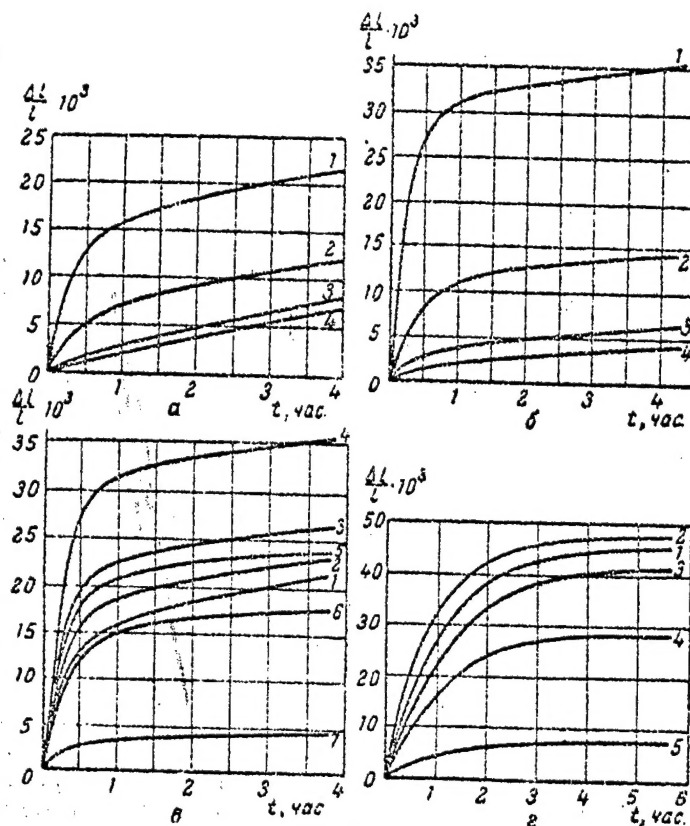


Fig. 1. Function of relative elongation  $\frac{\Delta l}{l}$  during creep in time  $t$  for samples Cu, Cu-Ni and Ni-Fe (temperature of test  $\approx 1000^\circ$ ,  $\sigma = 10 \text{ gm/mm}^2$ ):

- a - Cu; 1-  $\gamma = 0$ ; 2-  $\gamma = 15 \text{ min.}$ ; 3-  $\gamma = 1 \text{ hour}$ ; 4-  $\gamma = 4 \text{ hours}$ .
- b - 50% Cu - 50% Ni; 1-  $\gamma = 0$ ; 2-  $\gamma = 15 \text{ min.}$ ; 3-  $\gamma = 1 \text{ hour}$ ; 4-  $\gamma = 4 \text{ hours}$ .
- c - ( $\gamma = 0$ ) Cu-Ni:  
 1- Cu; 2- 90% Cu + 10% Ni; 3- 75% Cu + 25% Ni; 4- 50% Cu + 50% Ni; 5- 25% Cu + 75% Ni; 6- 10% Cu + 90% Ni; 7- Ni.
- d - ( $\gamma = 0$ ;  $T = 1100^\circ$ ) Ni-Fe:  
 1- Ni; 2- 75% Ni + 25% Fe; 3- 50% Ni + 50% Fe; 4- 25% Ni + 75% Fe; 5- Fe.

As is evident from figure 1a, with increased duration of preliminary annealing of the samples, creep elongation is reduced, principally at the expense of the reduction of the effect of the first stage becomes almost unnoticeable on the elongation curve. This provides the basis for the proposition that in the course of the first stage of creep the deformation is due to effects related to the non-equilibrium condition of the system which are eliminated as equilibrium is approached (reduction of the initial "activity" of the powder, possibly produced by excess vacancies and a correspondingly elevated coefficient of autodiffusi

This conforms with data presented in figure 2b concerning samples of a 50% mixture of Cu and Ni powders. As we know, intensive heterodiffusion processes occur in such samples at a high temperature, and due to unequal partial coefficients of diffusion a large excess of vacancies occurs which subsequently deposit out in the form of additional pores [5].

Sintering of powder mixture samples of mutually diffusible metals is worse in comparison to the sintering of pure components due to the occurrence of additional porosity. The curves of figure 2b show that the creep of a sample made of a 50% mixture of Cu-Ni powders is greatly increased under the influence of external forces in comparison to pure copper when  $\gamma$  is small ( $\gamma < 15$  min.). This effect must be due to the elevated value of the autodiffusion coefficient brought about by excess vacancies. In increasing the duration of preliminary delay  $\gamma$  to 4 hours creep elongation of a sample of a 50% Cu-Ni powder mixture is reduced and becomes less than for a sample of pure copper. From this we can conclude that during this delay the excess vacancies in this system disappear. Results of research on the kinetics of sintering lead to the same conclusion [4].

These effects find a non-contradictory interpretation only by treating the observed phenomenon as diffusion creep and on the contrary cannot at all be explained if we apply the concept of the "dislocation" theory of creep to them. Thus in conformity with the dislocation mechanism of plasticity following preliminary annealing, one would have to expect not a reduction but an increase in creep rate and a similar result for a sample made of a mixture of powders in which solid solutions are formed.

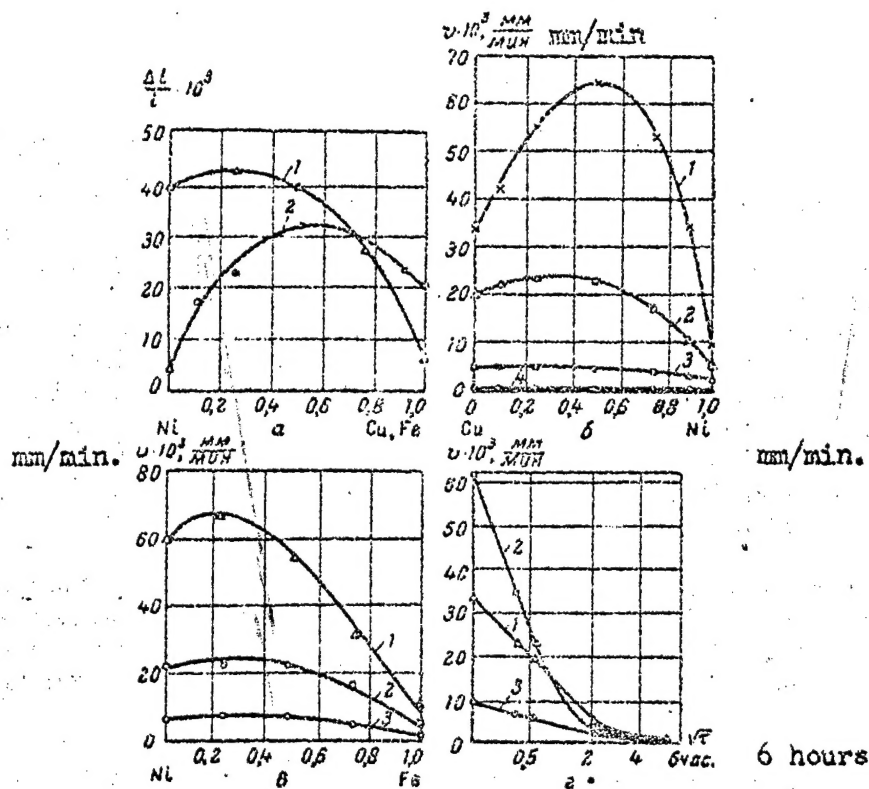


Fig. 2.

a - relationship of the concentration to full elongation  $\frac{\Delta l}{l}$  for 4 hours:

- 1 - Ni-Fe samples ( $T = 1100^\circ$ ,  $p = 50 \text{ gm/mm}^2$ ,  $\tau = 0$ );
- 2 - Cu-Ni samples ( $T = 1000^\circ$ ,  $p = 10 \text{ gm/mm}^2$ ,  $\tau = 0$ ).

b & c relationship of the concentration to initial rate of creep  $V$  for Cu-Ni and Ni-Fe samples following preliminary annealing of variable duration  $\tau$ :

b - 1 -  $\tau = 0$ ; 2 -  $\tau = 15 \text{ min.}$ ; 3 -  $\tau = 1 \text{ hour.}$   
(test temperature  $1000^\circ$ ,  $p = 10 \text{ gm/mm}^2$ ).

c - 1 -  $\tau = 0$ ; 2 -  $\tau = 15 \text{ min.}$ ; 3 -  $\tau = 1 \text{ hour.}$   
(test temperature  $1100^\circ$ ,  $p = 50 \text{ gm/mm}^2$ ).

d - relationship of initial creep rate  $V$  to the duration of preliminary annealing  $\tau$  for samples (temperature of test  $1000^\circ$ ,  $p = 10 \text{ gm/mm}^2$ ):  
1 - Cu; 2 - 50% Cu + 50% Ni; 3 - Ni.



Figures 1c and 1d show curves of creep elongation for samples made from differently proportioned mixtures of Cu-Ni and Ni-Fe powders. All these curves have  $\tau=0$  (i.e., the samples have not undergone preliminary annealing at high temperature). Samples of the Cu-Ni system were studied at a temperature of  $1000^\circ$  under a load of  $10 \text{ gm/mm}^2$ . In order to observe elongation values in samples made from a mixture of Ni and Fe powders it was necessary to elevate the test temperature to  $1100^\circ$  and to increase the applied stress to  $50 \text{ gm/mm}^2$ . In this as in the other system the greatest elongation with creep is seen in the samples of equal concentration, which, as has already been mentioned, is apparently due to the appearance of excess vacancies (increase in the autodiffusion coefficient) related to the dissimilar partial heterodiffusion of the components.

Figure 2a shows the relationship of complete elongation (creep over a 4 hour period) on concentration in samples of Ni-Cu and Ni-Fe powder mixtures. The extent of full elongation in each system is maximal at certain middle concentrations, as is apparent from figures 1c and 1d.

Data on the relationship of initial creep rate (in the start of the first stage) on the duration of preliminary delay  $\tau$  in samples of Cu-Ni and Fe-Ni powder mixtures are presented in figures 2b, 2c, and 2d. With small values of  $\tau$  there is an abrupt increase in the initial creep rate in samples of middle concentrations. With increase in  $\tau$  this effect becomes less significant and at large values of  $\tau$  ( $\tau > 4$  hours) it practically disappears. At large values of  $\tau$  the creep rate of a sample of a mixture of powders is about equal to the sum of the values for their components.

As has been shown, these relationships must be due to the effect of the occurrence of excess vacancies at the first stage of the exposure of powder mixtures of mutually diffusible metals to a high temperature and then the disappearance of the excess vacancies.

Above the phenomenon of creep in powder metal samples was viewed as occurring independently of the simultaneously occurring process of sintering. But either of these phenomena may have some effect on the other. This is evidenced by data on the relationship of contraction during sintering on the amount of stress applied, shown in figure 3a. As we can see, the amount of contraction is reduced with the increase in pressure applied. Quantitatively the effect is quite substantial. With a pressure of  $35 \text{ gm/mm}^2$  the contraction of copper over a four hour period at  $1000^\circ$  is reduced from 26% (in the absence of pressure) to 18%, i.e., by almost a third. It is possible that the suppression of sintering during strain deformation by creep is produced by a change in pore shape. Stretched out pores must produce less of a contraction during sintering

than isomeric pores of the same volume. Note that the observed decrease in contraction of the samples subjected to strain is approximately proportionate to the amount of creep elongation.

In order to test the influence of sintering on the course of creep the deformation of copper samples of different initial porosity was compared, subjecting them to strain at the same load and temperature. Figure 3b shows the curves for copper samples having the same initial porosity of 32% and 10% and subjected to testing at a load of 35 gm/mm<sup>2</sup> at temperatures of 900° and 1000°. In the absence of preliminary annealing ( $\tau=0$ ) the behavior of samples of different porosity varied, the more porous samples show even greater deformation. Following preliminary annealing ( $\tau=4$  hours), when the porosity of both samples has practically equilibrated, their behavior becomes identical. Apparently this phenomenon is entirely caused by a difference in the effective strain acting in samples of different porosity. In a porous sample there is a relative reduction of the cross-sectional area occupied by the substance by an amount  $2\approx 3/2\eta$ , in which  $\eta$  is porosity volume, for  $a$  is the part of the cross-section occupied by pores. Accordingly we can expect that in samples differing by 22% in porosity the effective pressure differs by 33%. Such a relationship completely explains the observed difference in the amount of deformation. Consequently there is no special effect of the contraction process on the course of creep.

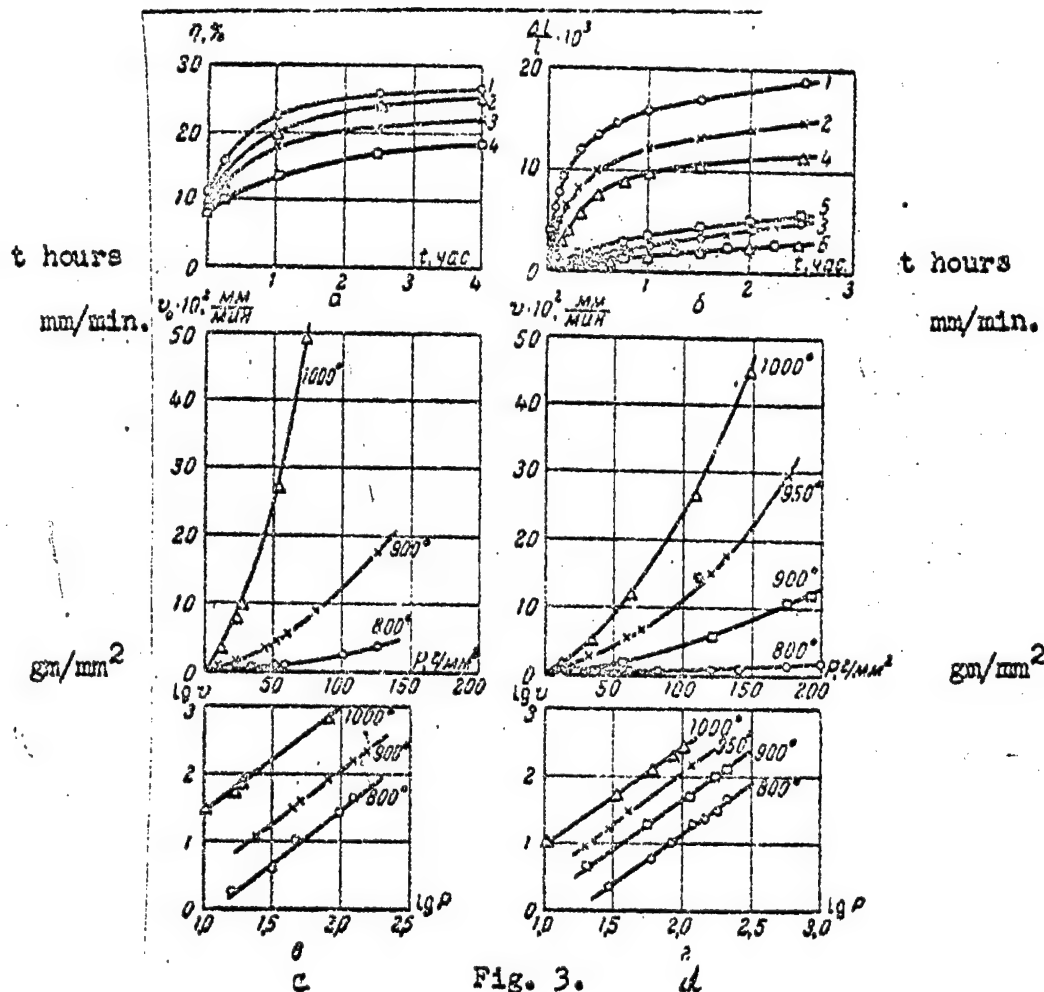


Fig. 3.

- a - curves of isothermal contraction of Cu samples (annealing temperature 1000°):  
 1-  $P=0$ ; 2-  $P=0.5$ ; 3-  $P=1$ ; 4-  $P=3.5 \text{ kg/mm}^2$
- b - relationship of relative elongation due to creep to time  $t$  for Cu samples of different initial porosity  $\eta_H$  (temperature of preliminary annealing 1000°): 1-  $\eta_H=32\%$ ;  $T=1000^\circ$ ;  $\tau=0$ ; 2-  $\eta_H=10\%$ ;  $T=1000^\circ$ ;  $\tau=0$ ; 3-  $\eta_H=32\%$ ; and  $10\%$ ,  $T=1000^\circ$ ;  $\tau=4 \text{ hours}$ ; 4-  $\eta_H=32\%$ ,  $T=900^\circ$ ;  $\tau=0$ ; 5-  $\eta_H=10\%$ ,  $T=900^\circ$ ;  $\tau=0$ ; 6-  $\eta_H=32\%$  and  $10\%$ ,  $T=900^\circ$ ;  $\tau=4 \text{ hours}$ ;
- c - relationship of initial creep rate  $v_0$  ( $\tau=0$ ) to pressure  $P$  at different temperatures; below is the same graph on logarithmic coordinates.
- d - relationship of the rate of steady creep  $v$  ( $\tau=4 \text{ hours}$ ) to pressure  $P$  at different temperatures; below is the same graph on logarithmic coordinates.

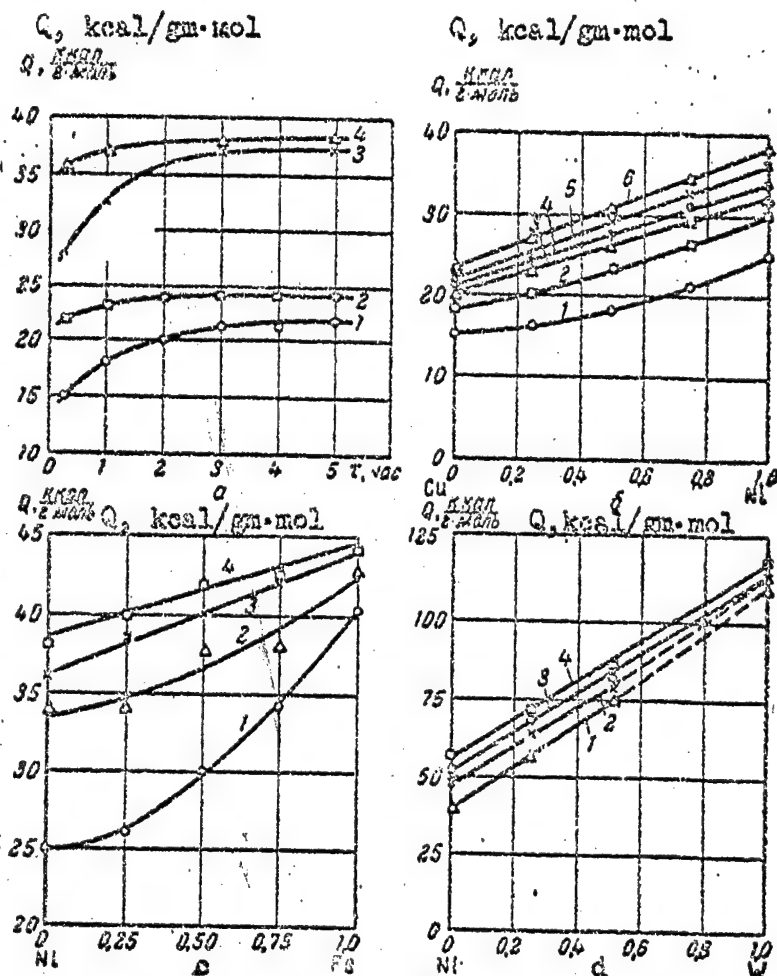


Fig. 4.

- a - Relationship of activation energy  $Q$  of creep to time  $t$  and preliminary annealing temperature  $T$  for Cu samples: 1, 3- first stage of creep (1-  $T=1000^\circ$ , 3-  $T=1060^\circ$ ); 2, 4- second stage of creep (2-  $T=1000^\circ$ , 4-  $T=1060^\circ$ );
- b, c, d - relationship of concentration on activation energy  $Q$  ( $T$  of preliminary annealing  $1000^\circ$ ) for various samples:
- b - 1, 2, 3- first stage of creep (1-  $t=0$ ; 2-  $t=15$  min.; 3-  $t=4$  hours); 4, 5, 6- second stage of creep (4-  $t=0$ ; 5-  $t=15$  min.; 6-  $t=4$  hours);
- c - 1, 2- first stage of creep (1-  $t=0$ ; 2-  $t=4$  hours); 3, 4- second stage of creep (3-  $t=0$ ; 4-  $t=4$  hours);
- d - ( $T$  of preliminary annealing  $1250^\circ$ ): 1, 2- first stage of creep (1-  $t=15$  min.; 2-  $t=4$  hours); 3, 4- second stage of creep (3-  $t=15$  min.; 4-  $t=4$  hours).

Some interest exists in explaining the relationship of creep rate and creep elongation to the applied pressure. Theoretically, for an equilibrium system in the event of the diffusion mechanism the creep rate should be a linear function of the force, i.e., it should be directly proportional to the pressure  $P$ . Calculations based on dislocation ideas usually assign a stronger dependence on  $P$  (for example, the ratio of the rate  $v$  to the value  $p^n$ , in which  $n=3$  or  $4$ , according to reference [2], or  $v \sim \text{Sh}P$  according to one investigation [6]).

In figures 3c and 3d we show the relationship of initial creep rate  $v_0$  (where  $\tau=0$ ) and the steady creep rate  $v$  (where  $\tau=4$  hours) to the pressure  $P$  at different temperatures for samples pressed from copper powder with an initial porosity of  $\sim 32\%$ . On the same figures we see the relationship of  $\log v$  to  $\log P$ . As can be seen,  $v = Ap^k$ , in which in the initial stage of creep  $k \approx 1.4-1.5$ , while in steady creep,  $k \approx 1.3$  at all temperatures. The non-linear relationship of  $v$  on  $P$  in this case cannot be viewed as contradicting the diffusion mechanism. The reason is that the powder metal samples studied are non-equilibrium systems. Even in the transition from the initial stage to steady creep the value of  $k$  is reduced, approaching unity. But even in the stage of steady creep the samples cannot be looked upon as having attained complete equilibrium.

This is evident from the data on the energy of activation of the creep process which are displayed in figure 4. The amount of activation energy  $Q$  was determined by the relationship of creep rate to temperature in which the relationship was thought to have the form [1]:

$$v = \frac{A}{T} e^{-Q/RT},$$

in which  $A$  is a constant and  $R$  is the gas constant.

Inasmuch as  $v$  depends on the time  $t$ , values of  $v$  in relation to temperature were used in determining  $Q$  which corresponded to one and the same  $t$ . Thus values of  $Q$  were found which corresponded to the initial rate of the first stage of creep as well as to the rate of steady creep. Values of  $Q$  are given in figure 4a for different stages of creep in samples of pure copper with respect to  $\tau$ , (the duration of preliminary annealing), in which determinations were made which correspond to preliminary annealing at temperatures of  $1000^\circ$  and  $1060^\circ$ . The values of  $Q$  obtained depended on  $\tau$  as well as on the temperature of preliminary annealing. But even the largest value of  $Q$ , following 5 hours of annealing at  $1060^\circ$ , is only 38,000 kcal/gm.mol, which is substantially less than the equilibrium value for the activation energy for volumetric auto-diffusion of copper, equal [7] to 48,000 kcal/gm.mol, and according to some data [8] even to 57,000 kcal/gm.mol. At the same time these values are much greater

than the activation energy of internal friction along grain boundaries, which in copper is 33,000 kcal/gm.mol [9], thus the existence of this process cannot be proposed. We know that a lowering of the activation energy of autodiffusion always obtains in non-equilibrium systems. It may, for example, be due to the presence of excess vacancies or to atoms displaced from equilibrium positions in which the activation energy for migration is reduced. It is possible that in the case of a non-equilibrium system an increased number of atoms experiencing diffusion displacements is involved with increasing pressures, because of which the creep rate increases abnormally with increased pressures. In view of the fact that according to creep kinetics the powder metal bodies studied must be considered as non-equilibrium bodies, a deviation of the linear relationship of  $\dot{\epsilon}$  on  $P$  is not excluded even in the diffusion mechanism of creep [See Note].

(Note: A dependence of  $Q$  on  $P$ , which has as yet not been verified, has also not been excluded. The values for  $Q$  given in figure 4 involve creep at a pressure  $P=1$  kg/cm<sup>2</sup> for the Cu-Ni system,  $P=5$  kg/cm<sup>2</sup> for the Fe-Ni system and  $P=3.5$  kg/cm<sup>2</sup> for the system Ni-W.)

As to a concentrational relationship of activation energy in mixed powder samples, the data on this are given in figures 4b, 4c and 4d. Here values for  $Q$  are also shown for the system Ni-W (fig. 4d) obtained in tests conducted at temperatures of 1100° and 1250° at a pressure  $P=3.5$  kg/cm<sup>2</sup> [See Note].

(Note: "Active" tungsten powder of grain size ~10 microns was used.)

As the data from figure 4 show, at prolonged periods of preliminary annealing the relationship of concentration to  $Q$  in the systems Ni-Fe, Ni-Cu and Ni-W approaches a straight line, which does not contradict a diffusion mechanism.

## CONCLUSIONS

1. The general course of deformation change with time in the case of creep of porous powder metal bodies (at high temperatures) does not differ from that of solid bodies. At first a stage of "unsteady creep" is observed in which deformation is attenuated with time, which is followed by a stage of steady creep with a constant deformation rate.

2. Preliminary annealing of powder metal samples reduces the amount of complete deformation in creep. The reduction is mainly due to a reduction in the deformation corresponding to the first stage of creep.

3. In powder metal samples made from mixtures of mutually diffusing metals during the initial moments of high temperature exposure the deformation related to the first stage of creep is greatly increased; with prolonged annealing the initial creep rate and the amount of complete deformation fall abruptly.

4. Deformation of a porous sample by stretching at high temperatures markedly delays sintering.

5. In samples of different initial porosity a different initial creep rate is found to correspond with different effective pressures.

After annealing, which equilibrates the porosity, the creep rate of the samples becomes the same.

6. There is more than a more straight line relationship of initial creep rate and steady creep rate to pressure applied in the case of powder metal bodies ( $v = p^k$ , where  $k = 1.5-1.3$ ), which is possibly due to divergence from the equilibrium state.

7. The amount of activation energy for the creep process (which determines the temperature function of creep rate) in single component powder metal bodies is lower than the equilibrium energy of activation for volumetric autodiffusion.

In the case of samples made from mixtures of different metal powders which were subjected to prolonged annealing the energy of activation of creep depends on the concentration of the mixture in a linear relationship.

8. These relationships can be explained only by the concept of the diffusion mechanism of creep, taking into consideration the presence of deviations from the equilibrium state in powder metal bodies.

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# CERTAIN PROBLEMS ON THE THEORY OF SINTERING AND CREEP

Following is a translation of an article by M. Yu. Bal'shin in the Russian-language book Issledovaniya po zharoprochnym splavam (Research on Heat-Resistant Alloys) Vol 4, Publishing House of the Academy of Sciences, USSR, Moscow, 1959, pages 311-316.

Sintering is a process of deformation (as is creep) due to forces of surface tension [1]. Accordingly sintering theory is a part of the general theory of deformation and sintering processes must be subject to the laws common to all deformation processes.

Certain common principles for slow deformation can be reduced to the following considerations [2].

1. Binding energies of a body can be equilibrated with the mechanical as well as the thermal energy of a body;
2. During deformation the thermal energy of every atom can be rapidly concentrated in sites of the disruption of its bond with other atoms.
3. Deformation of solid as well as liquid bodies is basically achieved by the sliding of atom layers (as in deformation along grain boundaries). The deformation rate is proportional to two factors (i.e., to their production) -- the number of layers taking part in the sliding process and the average rate of sliding for each atom layer.
4. For effective deformation it is necessary that the sliding be along mutually intersecting surfaces having higher boundary energy than other sliding segments. Hence the conditions for sliding are specified by those intersecting segments whose boundary energy is equal to  $2 Q_f$  i.e., to twice the latent heat of fusion  $Q_f$ .

Amorphous bodies (glass, for example) at sufficiently high temperatures can be looked upon in a first approximation as liquids of high viscosity. The number of layers in which sliding occurs does not depend on the tension  $\sigma$ , but the sliding rate of each layer is proportional to  $\sigma$ . Therefore the rate of relative deformation is also proportional to  $\sigma$  and is determined by the formula:

$$\frac{dl}{dt} = \frac{1}{\eta} \sigma, \quad (1)$$

in which  $l$  is the linear dimension of the body;  $\eta$  is the coefficient of viscosity, and  $\frac{1}{\sigma}$  is the yield coefficient.

In the case of crystalline bodies there are two temperature regions for slow yield (creep), and for certain materials there is only one. One region is the region of unlimited flow (not observed in all materials) in which the critical tension (creep limit, yield limit)  $\sigma_K \rightarrow 0$ . The region for the existence of unlimited flow is determined by the condition:

$$\Delta H_T \gg 2 Q_f \quad (2)$$

in which  $\Delta H_T = H_T - H_0$  ( $H_T$  is the heat content of the body at temperature  $T$ ;  $H_0$  is the heat content at  $0^\circ\text{K}$ ).

Henceforth, for brevity, we will call  $\Delta H_T$  simply the heat content (at temperature  $T$ ). The condition of formula (1) indicates that the energy of bond rupture  $2Q_f$ , which must be overcome in order to deform the body, can be completely equated to the heat energy of the body. Hence the latter will be deformed very slowly even when  $\sigma_K \rightarrow 0$ .

On the basis of formula (2) it is possible to calculate the critical temperature  $T_K$ , above which unlimited flow occurs. This temperature depends on the ratio  $\Delta H_f/Q_f$ , in which  $\Delta H_f$  is the heat content of a fluid body at  $T_f$ . In general, for the overwhelming majority of cases this ratio fluctuates between 6 and 2:

$$6 \gg \frac{\Delta H_f}{Q_f} \gg 2. \quad (3)$$

The larger this ratio, the smaller  $T_K$  is. If  $\frac{\Delta H_f}{Q_f} \leq 3$ , then  $T_K = T_f$  and consequently unlimited flow can be realized only at the temperature of melting and fusion of a portion of the material. Consequently such materials do not have a region of unlimited flow in the completely solid state. Among the pure metals this region is lacking for bismuth, antimony and tin. In table 1 the values of  $T_K$  are given for a number of pure metals in relation to the ratio  $\Delta H_f/Q_f$ . For most of the pure metals the value of  $T_K$  fluctuates within the limits of 55-80% [of  $T_f$ ]. In certain metals, for example aluminum, the value of  $T_K = 90\%$ . Solid compounds -- carbides, borides, nitrides and many other substances, for example ice, do not have a region of unlimited flow.

Table 1

Metal	$\frac{H_f}{Q_f}$	$H_f$ kcal/gm-at	$Q_f$ kcal/gm-at	$T_f - 273^\circ$ (°C)	$T_k - 273^\circ$ (°C)	$100 \frac{T_k}{T_f}, \%$
Chromium	5,9	21 550	3650	1350	914	58
Iron	5,17	18 850	3650	1539	754	57
Platinum	4,11	19 300	4700	1769	1236	74
Lead	4,04	4810	1190	327	140	69
Nickel	3,94	18 620	4220	1455	888	73
Silver	3,82	10 540	2890	961	643	72
Antimony	2,12	10 080	4750	831	631	100
Copper	3,66	11 340	3050	1083	797	72
Aluminum	3,16	7 880	2500	680	624	96
Cadmium	3,14	4 810	1530	321	296	96
Tin	2,71	4 550	1690	232	232	100
Bismuth	2,15	5 600	2600	271	271	100

Sintering can approach a limit (although only after an interminally large interval of time) only under conditions of unlimited flow of the material. Hence an obligatory condition for adequately effective sintering is to conduct the process at  $T \gg T_k$ , or to sinter with supplementary mechanical compression (under pressure or by vibration).

For many pure metals the temperature  $T_k$  corresponds to the temperature at the start of sintering according to Sauerwald's rule (66-80% of the absolute melting point). Actually Sauerwald's rule is not suitable for pure metals because the temperature at the start of effective sintering fluctuates from 55% to 100% of the absolute melting point. Hence the sintering of a great many materials -- certain metals, most solid compounds -- can be sufficiently effective only with supplementary mechanical compression.

In the region of unlimited flow the number of sliding atomic surfaces and the average sliding rate of each surface are proportional to  $\sigma$ . Therefore the general deformation rate is proportional to  $\sigma^2$ . Flow in such a relationship of deformation rate to tension may be termed quasi-viscous, and here the deformation rate can be determined by the formula:

$$\frac{dl}{dt} = \frac{\sigma}{\eta \sigma_{\max}} \sigma = k \sigma^2, \quad (4)$$

in which  $\sigma_{\max}$  is the pressure necessary for the maximal possible hardening of a material at the temperature given;  $\eta$  is the viscosity coefficient when  $\sigma = \sigma_{\max}$ ; and  $\frac{\sigma}{\eta \sigma_{\max}}$  is equivalent to the flow coefficient in formula (1).

In the region of limited flow when  $T < T_k$  there is a certain critical pressure (yield limit, creep limit)  $\sigma_k$ . At  $\sigma < \sigma_k$  a material with limited flow is not deformed. Hence effective sintering is possible here only with supplementary mechanical compression.

In this region the number of sliding atomic surfaces and the average sliding rate of each surface is approximately proportional to  $(\sigma - \sigma_k)$ . Therefore the general rate of deformation is proportional to  $(\sigma - \sigma_k)^2$ :

$$\frac{dl}{dt} = \frac{\sigma - \sigma_k}{\eta \sigma_{\text{max}}} (\sigma - \sigma_k) = k (\sigma - \sigma_k)^2. \quad (5)$$

As an approximation formula (5) can be expressed as:

$$\frac{dl}{dt} = \frac{\sigma^{m-1}}{\eta \sigma_{\text{max}}^{m-1}} \sigma = k \sigma^m, \quad (6)$$

in which  $m > 2$  and approaches this limit only at  $\sigma_k \neq 0$ .

The greater  $\sigma_k$  is, i.e., the higher the temperature and the less the dispersion, then the greater is the value for  $m$ .

The flow described by formula (5) and approximated by formula (6) at  $m > 2$ , is termed by us quasi-plastic flow. At  $m=2$  it becomes quasi-viscous flow.

It must, however, be borne in mind that in certain forms of deformation the degree of  $m$  can be somewhat larger than 2 even in the case of quasi-viscous flow in the region of unlimited flow because of a dimensional effect which impedes deformation in the case of an increase in the dimensions of the deformed segment.

With respect to deformation conditions the contact deformation of separate particles during sintering is closest to the contact deformation of bodies in the determination of heat hardness. Hence it is possible to make a model study of the sintering kinetics of separate particles by studying the impression change in the determination of heat hardness.

For quasi-viscous flow, according to formula (4) the kinetics of radius increase in the imprint of a spherical indenting agent is determined by the formula:

$$\frac{y^3}{F^2} \sim t, \quad (7)$$

and the diagonal  $y$  of the imprint of a pyramid in the determination on hardness according to Vickers is determined by the formula:

$$\frac{y^4}{F^2} \sim t, \quad (8)$$

in which  $F$  is the load and  $t$  is the duration of the load's effect.

According to formula (6), in the case of quasi-plastic flow with a spherical indenter:

$$\frac{y^{2m+2}}{F^m} \sim t \quad (9)$$

and with a pyramidal indenting agent:

$$\frac{y^{2m}}{F^{2m}} \sim t, \quad (10)$$

in which  $m > 2$ , the degree of equation (6).

A number of tests indicates (figure 1) that actually under conditions defined by formula (2) the relationships corresponding to formulas (7-10) do occur.

Since when  $y=0$  the pressure  $\sigma = k \frac{F}{y^2} = \infty$ , therefore rapid plastic deformation occurs first, which can, for example in the case of quasi-viscous flow with a pyramidal indenter, be calculated by the formula:

$$\frac{y^4}{F^2} \sim (t + t_0) \quad (11)$$

or approximated by:

$$y^n \sim t, \quad (12)$$

in which  $n \geq 4$ , and  $t_0$  depending on the temperature has a value (in quasi-viscous flow) from several minutes to hours.

Figure 1 confirms the correctness of formula (11).

The kinetics for the increase in the contact radius  $y$  between two spherical particles of radius  $a$  in quasi-viscous flow is:

$$\frac{y^4}{a^3} \sim t \quad (13)$$

and in quasi-plastic flow is:

$$\frac{y^{2m}}{a^m} \sim t, \quad (14)$$

in which  $m \geq 2$ .

Thus, as is also the case in the kinetics of long-term hardness, deformations are determined not only by slow creep but also by rapid plastic deformation, which also can be estimated by introducing the value of  $t_0$  into formulas (13) and (14). To illustrate:

$$\frac{y^4}{a^4} \sim (t + t_0) \quad (15)$$

or approximately:

$$\frac{y^n}{a^n} \sim t, \quad (16)$$

in which  $n > 4$ .

The value of  $n$  can also be somewhat increased due to increased resistance of the material to deformation, and with the volume of the material deformed.

According to the Pines-Kuchinskiy theory of diffusion,  $\frac{y^4}{a^4} \sim t$ . By increasing the particle radius  $\ell$  times, the sintering rate in quasi-viscous flow is increased by more than  $\ell^2$  times, and in the case of diffusion flow by somewhat more than  $\ell^3$  times.

From comparing formulas (13) and (15) it follows that the exponent in the case of  $\ell$  can be equal to 2 for quasi-viscous flow only in the time interval  $\Delta t = t_2 - t_1$ , i.e., in which  $\ell$  is in the formula:

$$\ell^m = \frac{d'}{d''} = \frac{\Delta t'}{\Delta t''}, \quad (17)$$

in which  $d'$  and  $d''$  are the linear dimensions of the particles and  $\Delta t'$  and  $\Delta t''$  are the time intervals required to bring corresponding temperatures from a uniform state  $A_1$  (for example 50% porosity or 10% contact) to another  $A_2$  (for example 20% porosity or 50% contact of particles).

In table 2 are the calculations based on Alexander and Baluffi's data [4] for the value of the exponent  $m$  of  $\ell$  in the case of copper wires sintered to uniform porosity with diameters  $d' = 128$  mm, and  $d'' = 52.6$  mm.

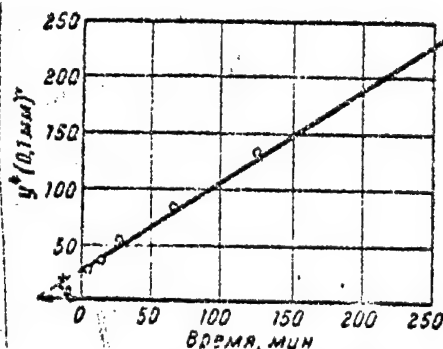
$y^4 (0.1 \text{ mm})^4$ 


Fig. 1. The kinetics for the change in the diagonal of the impression,  $y$ , for copper at a temperature of  $800^\circ$  and a load of 250 grams.

Table 2

Sintering temperature $^\circ\text{C}$	% porosity		$\Delta t'$ , hours	$\Delta t''$ , hours	exponent in formula (17)	average
	$A_1$	$A_2$				
900	7.8	6.0	96-18=78	10-2=8	2.51	2.42
1000	8.5	5.4	110-32=78	10-2=8	2.31	
1050	5.3	4.0	108-50=58	10-2=8	2.23	

Thus the average value of  $m$  is 2.42, closer to 2 than to 3. It must be taken into account that due to the significantly larger number of more active surface atoms in thinner particles the value of  $m$  must be somewhat greater than 3 in the case of diffusion and quasi-viscous flow. Hence the results in table 2 to a greater extent support the theory of quasi-viscous and not diffusion flow.

The flooding of a pore in the case of isolated deformation is not local as in the case of baking two particles, but occurs throughout the entire volume of the body. This fact substantially impedes deformation for its rate in this case is determined by the zone of slowest deformation. Thus during quasi-viscous flow the rate of flooding a

central pore of radius  $r$  in a body of radius  $R$  (the slowest deformation occurring in the zone of radius  $R$ ) at a surface tension of  $\gamma$  will be:

$$\frac{dr}{dt} \sim \frac{4\gamma^3}{r} \frac{r}{R} \sim \frac{4\gamma^3}{R}, \quad (18)$$

i.e., the greater the volume in which deformation occurs (the greater the value of  $R$ ), the less will be its rate; at  $R \rightarrow \infty$ ,  $\frac{dr}{dt} = 0$ . It follows from formula (18) that the speed of flooding is determined not by the size of the pore but by the dimensions of the body.

If it occurs in a body with many isolated pores then the rate is defined with a minimal value of  $\sigma$ . Since there are zones in which  $\sigma \rightarrow 0$ , then the time of deformation in the case  $\rightarrow \infty$ . This and not merely the effect of gases explains the practically absent closure of isolated pores during sintering.

Because of different deformation rates in different zones during sintering it is unavoidable not only that pore closure and increase of contacts take place, but also that new pores and breaking of contacts occur, as well as zonal differentiation. The latter can not only reduce the sintering rate but can also implement consolidation.

The sintering rate rapidly falls in time not only due to a reduced number of defects in powder particles but also as a result of the growth of contact surfaces and of the volume of zones in which deformations are localized. Rapid increase in the stability of the conglomerate being sintered also slows the sintering rate. Hence the absorption of gases and impurities onto particle surfaces can in many cases be facilitated by sintering. Deposition is somewhat diminished with an increase in the size of the bodies being sintered.



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PROPERTIES OF CHROMIUM CARBIDES AND POWDER  
METAL ALLOYS ON THEIR BASE

[Following is a translation of an article by V. V. Grigor'yeva and V. N. Klimenko in the Russian-language book Issledovaniya po zharoprochnym splavam (Research on Heat-Resistant Alloys) Vol 4, Publishing House of the Academy of Sciences USSR, Moscow, 1959, pages 317-322.]

Metal carbides of groups IV, V, and VI of the periodic table of the elements are used in technology for the manufacture of quite hard powder metal alloys, employed principally for metal cutting. The carbides of tungsten and titanium or their mixtures serve as the base for hard powder metal alloys.

Chromium carbide is employed in limited amounts for these purposes, usually in the form of small additives which increase the resistance of the carbides to oxidation. The amount of chromium carbide added, for example, to titanium carbide does not exceed 10%, because a larger concentration produces a very brittle alloy. This limits the use of chromium carbide to binary and ternary carbides, but its properties merit consideration.

Chromium carbide does not lag behind the other carbides in hardness, although it is less refractory, and it surpasses all other carbides in its resistance to oxidation. Another advantage is its small specific gravity, in which respect chromium carbide yields only to silicon carbide and titanium carbide. Table 1 compares some of the properties of the metal carbides [1, 2].

Chromium forms several carbides with carbon. At the present time the existence of three carbides of chromium is reliably established:  $\text{Cr}_{23}\text{C}_6$  or  $\text{Cr}_4\text{C}$ , containing 5.68% C;  $\text{Cr}_7\text{C}_3$ , having 9% C; and  $\text{Cr}_3\text{C}_2$  containing 13.33% carbon.

It is postulated that at a temperature above 2000° still another carbide of chromium exists --  $\text{CrC}$ , containing 18.75% C and decomposing on cooling into  $\text{Cr}_3\text{C}_2$  and C. The carbide  $\text{CrC}$  has not been successfully isolated by fusion in a closed atmosphere or in a vacuum or by recrystallization from the molten state [1]. Not  $\text{CrC}$ , but  $\text{Cr}_3\text{C}_2$  and free carbon are obtained in all the tests.

Table 1

## Properties of Carbides

Carbides	Melting Point °C	Density gm/cm <sup>3</sup>	Micro-hardness kg/mm <sup>2</sup> (load 50 gm)	Resistance to oxidation at 900° gm/m <sup>2</sup> for 1 hour
TaC	3900	14,5	1800	
NbC	3500	7,8	2400	205,0
ZrC	3530	6,9	2600	480,0
TiC	3140	4,9	3200	12,1
WC	2900	15,8	2400	1140,0
VC	2830	—	2800	—
W <sub>2</sub> C	2730	17,3	3000	—
Mo <sub>2</sub> C	2700	9,2	1800	—
SiC	Decomposes above 2000°	3,2	3200	—
Cr <sub>3</sub> C <sub>2</sub>	1895	6,68	2700	0,66

Table 2 shows the properties of the chromium carbides now known, which have been rather poorly studied. As is evident, the Cr<sub>3</sub>C<sub>2</sub> carbide is the most refractory and the hardest.

Table 2

## Properties of Chromium Carbides

Carbide	$\text{Cr}_{23}\text{C}_6$	$\text{Cr}_7\text{C}_3$	$\text{Cr}_3\text{C}_2$	$\text{CrC}$
Carbon content, Wt. %	5.68	9.00	13.33	18.75
Structure	Cubical face-centered	Hexagonal trigonal	Ortho-rhombic	Cubical face-centered
Type	$D_{4h}^{81}$	$C_{4v}^{3v}$	$D_{5h}^{10}$	NaCl
Number of atoms in the lattice:				
chromium.....	92	56	12	-
carbon.....	24	24	8	-
Lattice Constants:				
$A^\circ$ a.....	10.638	14.01	2.82	-
b.....	-	-	5.53	-
c.....	-	4.532	11.47	-
Density, $\text{gm/cm}^3$	7.0	6.9	6.68	-
Melting Point, $^\circ\text{C}$	1520	1760	1895	above 2000
Mean thermal expansion $\times 10^{-6}$ between $20^\circ$ and $800^\circ$ , $\text{m/m}^\circ\text{C}$	10.1	10.0	10.3	-
Microhardness, $\text{kg/mm}^2$ , (at a load of 50 gm)	1650	2100	2700	-
Weight increase for 1 hour at $900^\circ$ $\text{gm/m}^2$	1.1	1.1	0.66	-

The data published by Kieffer and Schwarzkopf [2] and Kieffer and Kälbe [3] for a microhardness of  $\text{Cr}_3\text{C}_2$  equal to  $1300 \text{ kg/mm}^2$  are in error. According to our measurements the microhardness of  $\text{Cr}_3\text{C}_2$  is  $2700 \text{ kg/mm}^2$ .

The carbides of chromium differ in their resistance to acids. It has been established [4] that after boiling in dilute hydrochloric acid

(1:1) for 20 hours  $\text{Cr}_{23}\text{C}_6$  is completely dissolved,  $\text{Cr}_7\text{C}_3$  loses 5200 gm/mm<sup>2</sup> in weight, and  $\text{Cr}_3\text{C}_2$  loses little weight. This difference has been used by us to separate  $\text{Cr}_3\text{C}_2$  from the other carbides.

Upon treatment with oxidizing acids little difference is noted between the carbides. The ability of the chromium carbides  $\text{Cr}_{23}\text{C}_6$  and  $\text{Cr}_7\text{C}_3$  to be passivated during treatment with hydrogen peroxide is used in the phase analysis of steels to separate cubic and trigonal carbides of chromium from cementite and binary carbides [5, 6]. In steel alloys only  $\text{Cr}_7\text{C}_3$  and  $\text{Cr}_{23}\text{C}_6$  have been detected and not  $\text{Cr}_3\text{C}_2$ .

The effect of chromium carbide on carbides of other metals has been investigated with respect to increasing the resistance of tungsten or titanium carbide to oxidation by the addition of chromium carbide. It has been found that at 1725° up to 51 Wt.% of  $\text{Cr}_3\text{C}_2$  is soluble in titanium carbide [9, 14]. Solubility of  $\text{Cr}_3\text{C}_2$  falls sharply with temperature reduction and at 1300° is about 4%. Oswald [8] shows that the orthorhombic carbide of chromium is dissolved in titanium carbide. It is not known whether titanium carbide dissolves other chromium carbides. Titanium carbide does not dissolve in chromium carbide.

In tungsten carbide (WC) chromium carbide is practically not dissolved, but mixed crystals are formed in  $\text{W}_2\text{C}$ . Tungsten carbide is somewhat soluble in chromium carbide [7]. As far as we know, the effect of chromium carbide on other carbides besides tungsten and titanium carbide has not been studied.

Carbides of chromium can be obtained in two ways: as powders from mixtures of chromium oxide and carbon black by carbonization in hydrogen at high temperatures or by melting. The higher carbide of chromium,  $\text{Cr}_3\text{C}_2$  can be obtained only as the powder by the carbonization of chromium oxide with carbon black, the content of free carbon or of the carbide  $\text{Cr}_7\text{C}_3$  depends on the conditions of the procedure. By melting  $\text{Cr}_3\text{C}_2$  and free carbon or a mixture of the carbides  $\text{Cr}_3\text{C}_2$  and  $\text{Cr}_7\text{C}_3$  is always produced.

We have established conditions for producing chromium carbide corresponding to the formula  $\text{Cr}_3\text{C}_2$ . This carbide is obtained from a dry stoichiometric mixture of chromium oxide and carbon black by carbonization at 1600° in hydrogen for 1-1.5 hours.

Table 3 shows the results of analyses for chromium carbide produced at different exposures of the mixture in the furnace.

Table 3

Exposure in hours at a temperature of 1600°	Composition of the chromium carbide produced (chemical analysis, %)			
	total chromium	total carbon	free carbon	$\text{Cr}_3\text{C}_2$
0.5	85.7	13.04	0.10	93.5
1.0	85.5	13.20	0.10	96.4
2.0	85.8	13.04	0.15	97.1
4.0	85.6	13.42	0.40	98.0

Under these conditions it is possible to obtain the higher carbide of chromium containing no more than 3% lower carbides and no more than 0.1-0.2% free carbon in the form of friable briquets of a glistening silvery color. Such a carbide is quite suitable for use as a base for powder metal alloys.

Industrially produced chromium carbide contains up to 35% lower carbides and up to 1% free carbon. In small amounts almost pure  $\text{Cr}_3\text{C}_2$  is obtained with no difficulty from chromium carbide prepared according to the procedure worked out by us. The lower carbides of chromium, amounting to 2-3%, are removed by boiling the carbide powder in dilute hydrochloric acid (1:1). After acid treatment the concentration of  $\text{Cr}_3\text{C}_2$  is 99.5%. Chromium carbide  $\text{Cr}_7\text{C}_3$  can be obtained by melting as well as by carbonization of chromium oxide. From a stoichiometric mixture of chromium oxide and carbon black in hydrogen at 1400° we obtained chromium carbide  $\text{Cr}_7\text{C}_3$  in the form of a fine gray powder containing about 4%  $\text{Cr}_3\text{C}_2$ .

V. N. Yeremenko and L. A. Gayevskaya obtained pure  $\text{Cr}_7\text{C}_3$  by melting in a helium atmosphere at reduced pressure (100 mm Hg). The carbon content in the furnace batch was somewhat larger than in a stoichiometric composition.

Figure 1 shows the relationship of the hardness of chromium carbide and titanium carbide to the testing temperatures. The tests were performed in a vacuum on the VIM-1 device. The samples tested were: titanium carbide produced by hot rolling at 2500°, chromium carbide  $\text{Cr}_7\text{C}_3$  (cast), and chromium carbide  $\text{Cr}_7\text{C}_3$  (hot rolled). The relative density of the samples was 0.97-0.98. It is evident from these curves that at temperatures from 500° to 1000° the hardness of chromium carbide exceeds that of titanium carbide.

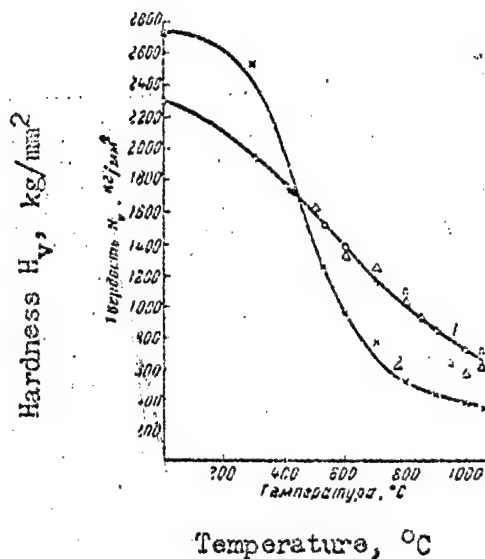


Fig. 1. Relationship of the hardness of chromium carbide (1) and titanium carbide (2) to testing temperatures.

Powder metal alloys on a base of chromium carbide possess the following valuable properties:

- 1) high hardness at room temperature and at high temperatures;
- 2) excellent resistance to oxidation;
- 3) resistance to corrosion;
- 4) resistance to abrasive wear.

The specific gravity of alloys is  $7 \text{ gm/cm}^3$ , which is half that of alloys in a base of tungsten carbide. The coefficient of linear expansion of the alloys approximates that of steel. The alloys are non-magnetic. Their resistance to bending at room temperature reaches  $73 \text{ kg/mm}^2$ , and at  $1100^\circ$  --  $40 \text{ kg/mm}^2$ . Note that at temperatures above  $1000^\circ$  the alloys are not creep-resistant. Compression strength at room temperature reaches  $73 \text{ kg/mm}^2$ .

The structure of an alloy with 15% nickel consists of carbide grains surrounded by a metallic phase lattice in a base of nickel. Alloys are pressed in the form of finished products or blanks of small dimensions from a powder mixture of chromium carbide and nickel and are sintered in hydrogen at a temperature above  $1200^\circ$ .

Mechanical processing of bars is possible after pressing and sintering at 900-1000°. Here provision must be made for contraction of the products after sintering, which is usually 17-20%. Following high temperature sintering the alloys can be worked only with abrasives. The alloys polish well and preserve their luster on heating to high temperatures.

An alloy based on chromium carbide was successfully employed by us as knife-edge fulcrums in buckle testing of powder metal samples with direct passage of current up to 1400°. In this case the fulcrums also served as conductors. Nozzles for sand-blasting machines were also manufactured from a powder metal alloy on a chromium carbides base and tested. Tests showed that such nozzles have a resistance to abrasive wear 15-20 times that of hardened steel.

The properties of the alloys depend on the composition of metallic and carbide phases which are formed by the reaction of carbides of chromium with nickel. In reactions with metals of the iron group the different chromium carbides behave dissimilarly, for example chromium carbide  $\text{Cr}_3\text{C}_2$  does not dissolve cobalt and nickel  $\text{Cr}_7\text{C}_3$  dissolves up to 6% nickel up to 26% cobalt and up to 40% iron.  $\text{Cr}_{23}\text{C}_6$  dissolves up to 6% nickel, 20% cobalt and 35% iron [10, 11, 12]. The solubility of  $\text{Cr}_3\text{C}_2$  in nickel and cobalt at 1250° reaches 12%, in iron -- 8% [13].

In the reaction of chromium carbide  $\text{Cr}_3\text{C}_2$  with nickel the separation of free carbon has been observed in alloys containing more than 10%  $\text{Cr}_3\text{C}_2$  by weight. The microhardness of the nickel phase in alloys of nickel with 10%  $\text{Cr}_3\text{C}_2$  is increased to 300 kg/mm<sup>2</sup> and is not changed on further increase of the  $\text{Cr}_3\text{C}_2$  content. Powder metal alloys on a chromium carbide base can be manufactured from  $\text{Cr}_3\text{C}_2$ ,  $\text{Cr}_7\text{C}_3$  or their mixture.

We have studied the effect of carbide composition on the mechanical properties of an alloy. Alloys were made from chromium carbide containing 3, 6.5, 11, 18 and 94%  $\text{Cr}_7\text{C}_3$  in a 15% compound of nickel. Buckling strength was tested at room temperature and at 1050° and 1100°. Sample size was 5x6x80 mm. The results of these tests are shown in figure 2. Of great interest is the increased strength at high temperatures due to an increased concentration of  $\text{Cr}_7\text{C}_3$  in the composition of the carbide. Resistance at room temperature, in contrast, is increased by increasing the concentration of  $\text{Cr}_3\text{C}_2$  in the carbide. Alloys with a high content of  $\text{Cr}_7\text{C}_3$  in the carbide are very brittle. The carbide phase composition also influences the hardness of alloys at high temperatures.



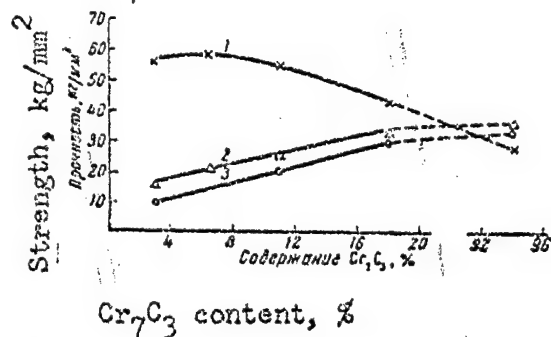


Fig. 2. Relationship of bending strength of alloys based on chromium carbide to the carbide compositions:  
1- at 20°; 2- at 1050°;  
3- at 1100°.

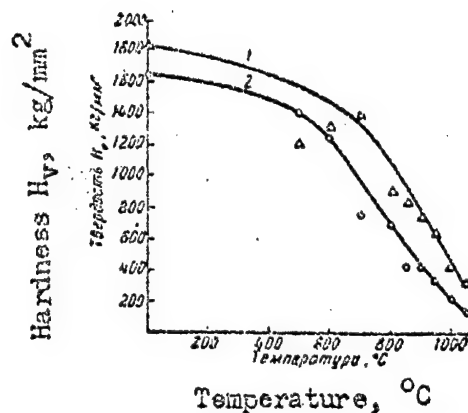


Fig. 3. Relationship of the hardness of an alloy on a chromium carbide base to testing temperatures:  
1- alloy in a base of Cr<sub>7</sub>C<sub>3</sub>;  
2- alloy in a base of Cr<sub>3</sub>C<sub>2</sub>.

Alloy samples were made from chromium carbide Cr<sub>3</sub>C<sub>2</sub> containing 6.5% Cr<sub>7</sub>C<sub>3</sub> and from chromium carbide Cr<sub>7</sub>C<sub>3</sub> containing 6% Cr<sub>3</sub>C<sub>2</sub>. The metallic composition of each alloy was 15% nickel. Relative density of the samples was 0.95-0.98.

Tests at temperatures from 20° to 1050° show that the hardness of the alloy based on Cr<sub>7</sub>C<sub>3</sub> is higher than the hardness of the alloy with the Cr<sub>3</sub>C<sub>2</sub> base (figure 3). The explanation for the increase in hardness and strength at high temperatures of the alloys made from the Cr<sub>7</sub>C<sub>3</sub> base will be the subject of further research.

#### CONCLUSIONS

1. Conditions are established for the production of chromium carbides Cr<sub>3</sub>C<sub>2</sub> and Cr<sub>7</sub>C<sub>3</sub> suitable for the manufacture of powder metal alloys based on chromium carbides.

2. The hardness of chromium carbide at temperatures from 500° to 1100° exceeds the hardness of titanium carbide.

3. With increased content of Cr<sub>7</sub>C<sub>3</sub> in the carbide hardness and bending strength are increased at high temperatures.

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PRODUCTION OF POWDERS OF ALLOYS BY THE METHOD  
OF DIFFUSION SATURATION

Following is a translation of an article by I. M. Fedorchenko and N. A. Filatova from the Russian-language book Issledovaniya po zharoprochnym splavam (Research on Heat-Resistant Alloys), Vol 4, Publishing House of the Academy of Sciences USSR, Moscow, 1959, pages 352-359.

Due to the continual growth of utilization parameters of components, power machinery and technological equipment for operation at elevated temperatures and pressures, in aggressive environments, and under high static and dynamic loads, it more and more becomes necessary to employ complex alloys which are stable under critical working conditions.

It is not always possible to obtain the results desired when manufacturing such alloys by the methods of powder metallurgy, by pressing and sintering products from a powder mixture of pure metals corresponding to the desired final composition of the complex alloy. This is due to the difficulty of producing the necessary homogeneity of structure and to the marked alteration in the shape of articles due to contraction. In order to obtain a higher degree of structural uniformity sintering must be conducted at elevated temperatures. These drawbacks appear to be less marked if powders are used as the starting material which have previously been alloyed in an initial state before objects are pressed from them.

At the present time the following methods are known for producing metal alloys as powders: electrolytic precipitation, vortex milling, spraying of molten metal and joint reduction of oxides.

The production of powders by electrolysis is limited by the relatively small number of elements possible and the relatively narrow limits of the composition of alloys produced. Manufacture of powders by vortex milling requires complex equipment and starting material in the form of shaving or wire. Powders produced by these methods are cold hardened and require annealing, which is a real drawback, for annealing powders composed of elements possessing hard to reduce oxides involves many difficulties. Spraying of molten metal is not always possible due to the complex technology. Joint reduction of oxides can be done in the production of powders from readily reducible oxides. Thus all the methods enumerated

possess their limitations and drawbacks, which make it necessary to develop new methods in order to expand industrial potentials of powder metallurgy.

In order to produce powder alloys composed of such elements as chromium, aluminum and titanium in this work we made use of the method of diffusion saturation of the starting powder in solid fills or through a gas phase. The method of thermodiffusional saturation in solid fills was selected because of the simplicity of engineering and equipment and the safety of operation, and the method of metal saturation through a gas phase was selected because of the rapid rate of the process. By these methods we have produced alloys on bases of nickel, molybdenum and iron with various concentrations of chromium, aluminum and titanium.

Powders of nickel, molybdenum and iron, and powders of a nickel-molybdenum alloy (80% nickel and 20% molybdenum), obtained by the joint reduction of their oxides, were utilized as starting materials.

#### Research on the Process of Diffusion Saturation of a Powder

Component powders, consisting of fine (less than 0.1 mm) powder particles of the diffusing metal and alumina annealed at 1400° and ammonium chloride dried at 80° were mixed in a ball mill. Chosen on the basis of research data [1,2], the fill consisted of 47.5% of one or several diffusing metals in equal quantities, 47.5% of aluminum oxide and 5% of ammonium chloride.

The pattern for packing the powder in the container is shown in figure 1. The fill was packed in the bottom of the container, then the batch of metal powder was poured and covered with a second fill and packed again. The thickness of the powder metal layer was 10-25 mm. The lid of the container was welded or plastered with a mixture of refractory clay and liquid glass.

The aluminum process was done at temperatures of 800° and 900°, the chromium and titanium processes were done at 800°, 900°, 1000° and 1100°. The duration of the chemico-thermal processing of the powder was 3, 4 and 6 hours.

As a result of these tests we obtained powder alloys of nickel, molybdenum, iron and nickel-molybdenum alloy with different concentrations of the alloying elements. The chemical analysis of averaged samples of these alloys is given in table 1.

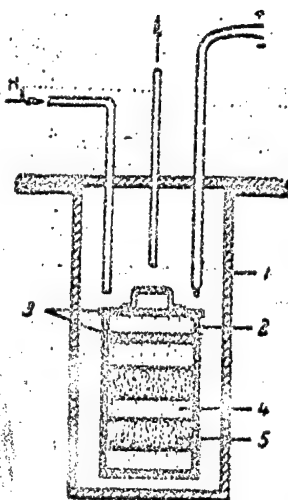
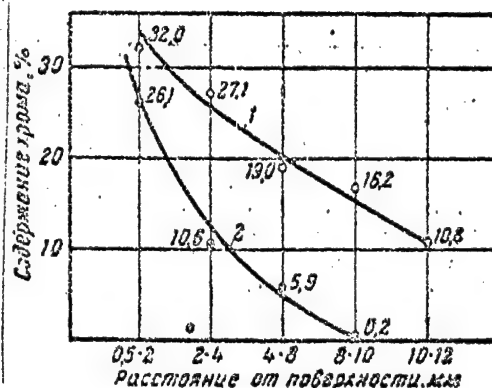


Fig. 1. Pattern of packing powder in the container:  
1- muffle; 2- crucible;  
3- lids; 4- diffusing mixture; 5- sponge or powder

Chromium content, %



Distance from the surface, mm

Fig. 2. Change in concentration of the alloying element with respect to the size of the powder layer ( $1000^{\circ}$  - 4 hours):  
1- for coarse powder; 2- for fine powder.

Table 1

## Chemical Analysis of the Materials Produced

Starting powder	Processing temperature °C	Processing time, hours	Content alloying elements	%
Nickel	900	3	Titanium	11.7
	900	4	Chromium	5.6
	1100	6	Chromium	28.3
Nickel-molybdenum alloy	900	6	Chromium	24.8
	1000	4	Titanium	16.2
	900	6	Aluminum	12.4
	900	6	Chromium	14.6
			Aluminum	5.3
Iron, produced by re- duction of the sinter with gas (coarse) 66666	900	6	Aluminum	14.3
	1000	4	Chromium	33.5
Iron, produced by re- duction of the sinter with gas (fine)	1000	6	Chromium	26.0

Intense sintering develops during this method of powder saturation, especially in the case of finer powders. A layer by layer chemical analysis of the materials produced showed a sharp change in concentration for the alloying elements varying with the thickness of the layer, which is especially marked for fine powder (fig. 2).

The non-uniform saturation of powder layers with depth is obviously due to insufficient layer permeability, which falls considerably with the growth of pores in the external layer of the powder.

#### Research on the Process of Diffusion Saturation of Highly Porous Sponge

The task of increasing layer permeability of the powder in the process of diffusion saturation was resolved with the use of a specially prepared highly porous sponge produced by sintering a mixture of the corresponding metal powder and ammonium bicarbonate (in a ratio of 3:1)

in a hydrogen atmosphere for two hours at temperatures of 800°-900°. During the sintering process some desulfurization and end-reduction of the powder and complete burning of the carbon took place.

Analysis of the sponge obtained showed that it has adequate strength, is not broken up during packing of the container and has a porosity of 80-85% with open intercommunicating pores. This sponge structure assures good permeability of the gases during the chemico-thermal process.

Diffusion saturation was performed on sponge prepared from pure powders of nickel, iron, and molybdenum as well as from powdered nickel-molybdenum alloy produced by joint reduction of oxides. The chemical composition of the starting powders is shown in table 2.

Table 2

Chemical Composition of Starting Powders							
Powder	Percentage of elements						
	C	S	P	Mn	Si	Cu	Mo
Nickel	0	0.003	-	-	0.01	0.003	-
Iron	0	0.005	0.012	0.25	0.05	-	-
Ni-Mo alloy	0	0.002	0.2	-	0.008	0.003	19.5
Chromium	0.03	0.015	-	-	0.4	-	-

In filling for diffusion saturation the packing of sponge into the container was done in the same way as the packing of powder in free fill. The chemico-thermal processing of the sponge was conducted over a wide temperature range (700°-1200°) at different duration.

In order to obtain the most uniform distribution of the alloying element with respect to the thickness of the layer, tests were done to determine the optimal thickness of the sponge layer. For this purpose sponge made of powders of different coarseness was taken and subjected to chromium processing at 900° for 6 hours. In order to determine concentration drops with respect to layer size, a layer by layer chemical analysis of the material obtained was performed. For the analysis the sponge obtained was longitudinally cut into two equal parts, one of which was longitudinally divided into five equal parts. The content of diffusing element in each layer obtained was determined. The results of chemical analysis are shown in table 3.

According to chemical analysis the sponge from the chromium process contains 32.8% Cr. The briquets made from other metal powders also had a uniform cross-section following the chromium diffusion process. The

porosity of the chromium-processed sponge, by estimation, fluctuated in the limits of 60-65%. In all the tests we obtained a light gray friable sponge which was easily ground into a powder.

From these data (table 3) it is evident that in order to produce a powder more uniform in chemical composition the thickness of the sponge layer made from fine powder particles must not exceed 15 mm, and in the case of coarse powders — 30 mm. A more uniform chromium distribution with respect to the thickness of a sponge layer is obtained by making the sponge from coarse powders. The chemical composition of some alloys produced by the method of chemico-thermal processing is shown in table 4.

Analogous tests for porous sponge saturation were performed by using a gaseous method of chromium diffusion. As is known, the process of chromium diffusion in a gaseous medium is most intense because of the greater rate of chromium transport to the surface being saturated [6,7], although this process also requires complex equipment and qualified personnel. Sponge made from nickel, iron and nickel-molybdenum powders was subjected to gaseous chrome diffusion. The hydrogen chloride needed in the tests was generated by the reaction of sulfuric acid on hydrochloric acid, passed through a dessicator and fed as a continuous stream into a tubular furnace.

Table 3

Results of a Layer by Layer Chemical Analysis of Sponge

Starting Powder	Thickness of sponge layer, mm.	Amount of chromium in layers, %				
		1	2	3	4	5
Nickel, particle size less than 0.25 mm	10	32.4	31.0	30.6	30.0	28.3
	30	31.6	30.0	29.7	26.0	23.2
Nickel, particle size less than 0.105 mm	15	28.7	23.0	19.2	10.8	6.0
	30	26.1	20.6	16.5	6.0	0.2
Iron, reduced from powder of sinter by gas (fine)	15	38.2	37.4	35.6	32.1	31.0
	30	33.2	30.7	28.5	20.7	15.1
Iron, reduced from powder of sinter by gas (coarse)	15	44.8	43.6	41.9	40.0	39.1
	30	37.2	38.3	30.0	26.7	22.3



Table 4

## Chemical Composition of Materials Produced

Starting Powder	Conditions for chemico-thermal processing		Amount of element alloyed according to chemical analysis	
	Temperature °C	Time hours		%
Iron	800	6	Aluminum	10.1
	900	6	Aluminum	14.7
	1000	6	Chromium	32.4
	1100	6	Chromium	46.3
Nickel	900	6	Chromium	24.6
	1000	4	Chromium	26.9
Nickel-molybdenum (Ni-80.4%, Mo-19.6%)	900	4	Chromium	25.2
	900	6	Aluminum	5.6
			Chromium	16.2
	1000	5	Titanium	19.8
Molybdenum	1000	4	Chromium	18.7
	1000	8	Chromium	24.3

For the chemico-thermal procedure pieces of sponge were cut which were of a diameter equal to the diameter of the tube in which the tests were done and of a thickness of 50 mm. These were placed in series in the tube of the furnace at some distance from one another. Gaps between the sponge samples were filled with fine pieces of chrome intermixed with foam chamotts. This arrangement of the sponge made it possible for gas to flow through it and consequently improved the conditions for gas saturation.

Chromium diffusion was performed at different regimes in which temperature (700-1200°) and time 1-20 hours) were varied, as well as the amount of hydrogen chloride fed into the reaction chamber of the furnace. In order to remove chloride residues before completion of the saturation process a stream of highly dessicated hydrogen was introduced into the reaction chamber of the furnace, which reduced the chlorides to the metal, the chlorine being removed from the furnace in the form of hydrogen chloride. In some cases the powder produced was washed in alcohol or in hot running water with subsequent drying [8].

It was found that by using highly porous sponge with the gas saturation method it is possible to produce a uniform distribution of chromium as regards the thickness of the layer, which makes possible the production of a powder alloy of uniform chemical composition. With this

method, for example, we were able to produce alloys of nickel -- molybdenum -- chromium of different chromium concentrations, as to the uniformity of their chemical composition, average chromium concentration in the sponge was 23.6% while in the center of a layer it was 22.0%.

#### Investigation of the Properties of Powder Alloys

The powders produced were subjected to investigation of their structure and hardness and to engineering tests. In order to determine phase composition, powders of nickel-chromium and iron-chromium alloys made by chromium diffusion of sponge at 900° for 6 hours were subjected to x-ray structure analysis. The powders used for the analysis had a chromium content of 17.2 and 13.4%.

[3,4] From system diagrams for nickel-chromium and iron-chromium alloys it is seen that alloys with this chromium content in both cases lie in the single-phase region for solid solutions of chromium in nickel or iron.

Interpretation of the x-rays taken of these materials in a Debye type chamber indicated complete correspondence with the system diagrams for these alloys. X-ray structure studies confirmed the presence of single-phase solid solutions and showed that the average lattice parameter for the nickel-chromium alloy is 3.53 Å and for the iron-chromium alloy - 2.86 Å.

Metallographic study of the structure of the alloys produced was done on samples pressed from the powders and subjected to sintering at 1200° for 2 hours in an atmosphere of highly dessicated hydrogen or in a fill of a completed diffusion mixture. In the latter case packing of the samples was done in the same way as packing of the sponge in chemico-thermal processing.

Metallographic study of ferrochrome containing 13.4% chromium and a nickel-chromium alloy with 17.2% Cr showed a monophasic structure of the alloy, which is a solid solution on an iron base. The findings on metallographic analysis correspond well with the results of x-ray structure study and with the diagrams of the states corresponding to binary systems.

Particle form has a substantial effect on the engineering properties of powders and on the mechanical properties of finished products.

Nickel and iron powders have a spongy structure with a highly developed surface. In powders subjected to the chemico-thermal process we see leveling of the surface and coagulation of particles. However as studies have shown, such a change in particle form does not lead to an abrupt change in extrudability of the powder. Particle microhardness makes it possible to evaluate not only the hardness of a given material

but also the uniformity of the properties of separately taken powder particles in order to obtain a uniform alloy and to compare it with the hardness of the source material. Particle hardness was determined on the microdurometer PMT-3 with a diamond pyramid at a load of 20 gm. Comparative data on the hardness measurements of starting and finished powders based on measurements of 5-10 particles of each powder are presented in table 5.

Table 5

Powder	Measurements of Particle Microhardness		
	Particle microhardness		Average microhardness
	kg/mm <sup>2</sup>		
	from	to	kg/mm <sup>2</sup>
Ferrochrome	211.0	291.2	220.0
Ferroaluminum (14.2% Al)	168.4	314.7	236.6
Nichrome (28.9% Cr)	124.8	241.0	174.9
Iron	124.0	233.2	137.4
Nickel	118.8	159.6	145.8

From published data [5] it is known that the hardness of diffusion layers of chromium produced during chemico-thermal treatment of iron does not differ sharply from the hardness of the base material. This is also confirmed for the production of powder alloys, whose microhardness is lower than the microhardness of cast alloys of the same composition, but somewhat higher than the microhardness of the starting powders. Thus, from the data in table 5, we see that the average hardness of iron powder particles is 137.4 kg/mm<sup>2</sup>, and of ferrochrome (33.8% Cr) — 220.0 kg/mm<sup>2</sup>.

In making products by the powder metal method the extrudability of the powder is one of the most important characteristics, affecting the strength not only of the extrusion but also of the sintered product. In order to elucidate the engineering characteristics of the powders obtained and the effect of the alloying element, a study was made of the extrudability of alloy powders in comparison with the extrudability of the material comprising the basis of the given alloy, for example nichrome with nickel, ferrochrome and ferroaluminum with iron, and nickel-molybdenum-chromium with nickel-molybdenum.

For this purpose cylindrical shapes with a  $\phi$  of 8 mm and weight of 3 gm were extruded at various pressures in the interval from 1 to 5 t/cm<sup>2</sup>. Extrusion was performed with lubrication of the walls of the press-form with cylinder oil.

Table 6 shows the results obtained, namely that the powders possess good extrudability in the entire interval of pressures.

Table 6

Relationship of Sample Porosity to Extrusion Pressure					
Extrusion Pressure t/cm <sup>2</sup>	Porosity of Powder Briquets, %				
	Reduced from	Iron-chrome (20.12% Cr)	Iron-Aluminum (9.0% Al)	Nickel	Nickel chrome (22.76% Cr)
1	40.0	42.5	41.3	43.3	44.1
2	26.3	28.0	28.6	30.3	34.2
3	19.2	21.5	22.3	23.8	26.6
4	14.3	16.6	18.0	19.0	22.5
5	10.6	13.4	12.5	15.5	19.4

These powders make strong briquets even at small (1 t/cm<sup>2</sup>) extrusion pressures, in which powders of the same chemical composition produced by other methods are not pressed.

#### CONCLUSIONS

1. Use of highly porous sponge as the starting material permits the production of powder alloys of complex chemical composition in a thickness layer up to 10-30 mm by the method of chemico-thermal diffusion saturation of active fills or of a gas phase.
2. The chemico-thermal method of diffusion saturation can be recommended for the production of powder alloys on a base of iron, nickel, molybdenum and other metals with metals possessing hard-to-reduce oxides (Cr, Al, Ti and others).
3. Powder alloys produced by the diffusion saturation method possess adequate uniformity for practical use and good engineering properties.
4. Refinement of the material takes place during the chemico-thermal process. Thus in the ferrochrome powder produced at 1000° for 6 hours C, S, Mn and Si were not detected.

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